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Wide band gap characteristic of quaternary and flexible Mg and Ga co-doped ZnO transparent conductive thin films

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ABSTRACT

Transparent conductive and flexible Mg and Ga co-doped ZnO (MGZO) thin films were prepared on polyethylene terephthalate (PET) by RF magnetron sputtering technique at room temperature. The effects of different working pressures on the structural, chemical, morphological, optical and electrical properties of MGZO thin films were investigated. X-ray diffraction results indicate that all the MGZO thin films were grown as polycrystalline wurtzite structures without secondary phases such as MgO, Ga_2O_3, $MgGa_2O_4$, or $ZnGa_2O_4$. The MGZO thin film prepared at 6 mTorr has the lowest value of full width at half maximum. A typical survey spectrum of all the MGZO thin films confirmed the presence of Mg, Ga, Zn and O. The MGZO thin film prepared at 6 mTorr showed the widest optical band gap energy of 3.91 eV and lowest electrical resistivity of $5.3 \times 10^{-3}\ \Omega$ cm.

1. Introduction

Light-weight and flexible electronic devices have been promising candidates for future portable product applications, such as thin-film solar cells, liquid crystal displays (LCDs), organic light-emitting diodes (OLEDs), electronic paper, and touch screen panels [1–3]. These flexible electronic devices require characteristics such as high transmittance in the visible region, wide band gap energy, and low resistivity for the thin transparent conducting oxide (TCO) layer in order to achieve high performance [4]. It is known that TCO thin films deposited on flexible substrate present limitations regarding substrate temperature, and large differences in the thermal expansion coefficients between TCO materials compared to that deposited on glass or single-crystal substrates [4]. Generally, indium tin oxide (ITO)-based thin films are the most widely used due to their excellent transmittance and low resistivity [5–9]. However, ITO-based TCO thin films suffer from several drawbacks, such as the high cost of In, and poor thermal and chemical stability [10]. ZnO-based materials are a promising alternative, because of their low cost, relatively low deposition temperature, outstanding electro-optical properties and stability in hydrogen plasma [6]. Un-doped ZnO thin films showed a relatively high resistivity ($10^{-2}\ \Omega$ cm) and optical band gap energy (3.3 eV). The electrical and optical properties of ZnO-based materials need to be improved by introducing Mg or Group III elements to the ZnO structure [11].

Among the various Group III elements, Ga-doped ZnO (GZO) thin films have indicated the best electrical and optical properties due to the fact that Ga is more resistant to oxidation, and has a similar ionic radius to those of Zn^{2+} ions, which minimizes the ZnO lattice deformations, even at higher concentration [6–8]. Previous research on GZO thin films indicated a lowest electrical resistivity of $1.4 \times 10^{-4}\ \Omega$ cm and widest band gap energy of 3.6 eV [11]. On the other hand, the electrical properties of GZO thin films on flexible substrates were worse than those deposited on glass substrates ($3.0 \times 10^{-3}\ \Omega$ cm). Gong et al. and Ahn et al. reported improvement in the electrical properties (below $5.0 \times 10^{-4}\ \Omega$ cm) of flexible GZO

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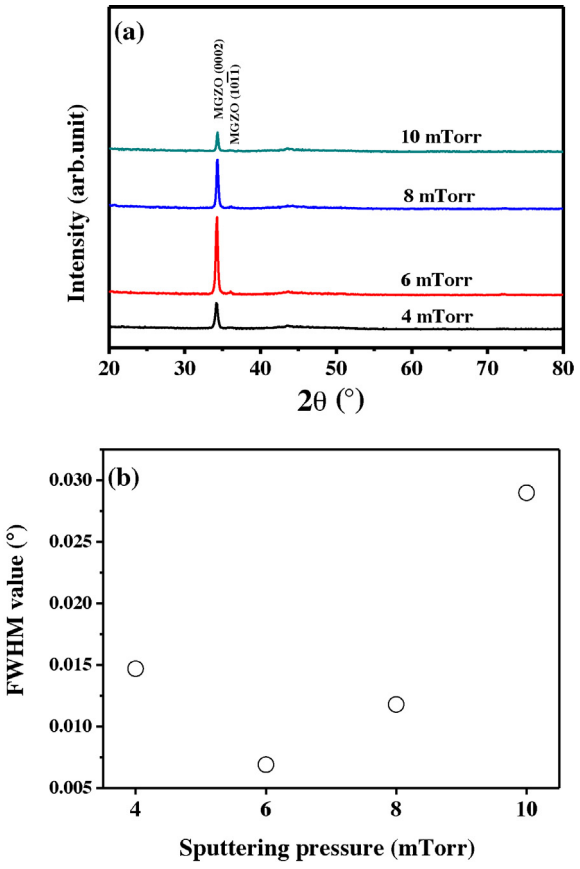

Fig. 1. XRD patterns (a) and FWHM values (b) of flexible MGZO thin films prepared with different working pressures.

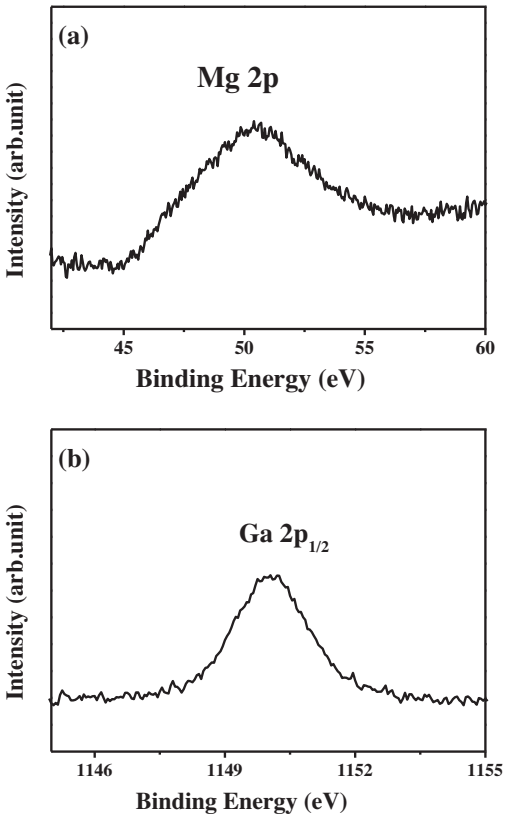

Fig. 2. High-resolution XPS spectra of the typical MGZO thin film prepared at 6 mTorr: core level spectrum for Mg 2p (a) and Ga 2p (b).

thin films prepared by introducing an SiO_2 buffer layer between GZO thin film and a flexible substrate [3,12]. Although outstanding electrical characteristics of GZO thin films were indicated, the band gap energy was limited to 3.6 eV, which resulted in poor performance for flexible devices.

Alternatively, MgO is a promising material for controlling the optical band gap of a ZnO crystal system [13]. Previous research showed that the band gap of Mg-doped ZnO (MZO) thin films can be controlled from 3.3 eV to 4.0 eV without changing the crystal structure [14,15]. Although MZO thin films showed wide band gap energy and n-type conductivity characteristics, they have a high electrical resistivity over $10^5\ \Omega$ cm, indicating limited applicability in electro-optical applications. Recently, Mg and Ga co-doped ZnO (MGZO) thin films that maintain a low electrical resistivity of less than $10^{-4}\ \Omega$ cm and wide band gap energy of over 3.75 eV were reported [14]. These studies suggested the possibility of preparing flexible TCO thin films with wider band gap energy and lower electrical resistivity characteristics by simultaneously introducing Mg and Ga co-doping in the ZnO structure.

This paper reports on MGZO thin films deposited on poly-ethylene terephthalate (PET) by RF magnetron sputtering technique at room temperature. The effect of different working pressures ranging from 4 mTorr to 8 mTorr on the structural, chemical, morphological, optical and electrical properties of MGZO thin films was studied.

2. Experimental details

MGZO thin films were prepared on PET by RF magnetron sputtering technique at room temperature. ZnO, MZO and MGZO ceramic targets were prepared using a conventional solid-state reaction method. A mixture was made from high-purity ZnO (Kojundo, 99.99%), Ga_2O_3 (Kojundo, 99.99%) and MgO powders (Kojundo, 99.99%), and pressed using a cold isostatic press followed by sintering at 1100 °C for 4 h in the furnace. The Mg and Ga concentrations were fixed to 5 at% and 3 at%, respectively. Prior to the deposition of MGZO thin films, the PET substrates were cleaned ultrasonically with isopropyl alcohol and deionized water for 10 min, sequentially. The cleaned substrates were dried with N_2 gas flow (99.99%) before being introduced into the sputtering chamber. The chamber was evacuated to a base pressure of 4.9×10^{-6} Torr. High-purity Ar gas (99.99%) was used as the plasma source, and the gas flow rate was controlled to 40 sccm using a mass flow controller. An RF power of 175 W was used for deposition. The working pressures of the deposited thin films were varied from 4 mTorr to 8 mTorr. The thicknesses of deposited thin films were fixed at 500 nm.

The crystal structure of the deposited thin films was examined by high-resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and 30 mA using Ni-filtered Cu K_α radiation [$\lambda = 1.54056$ Å]. The chemical binding energy and atomic ratios of the deposited thin films were confirmed by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, ThermoVG Scientific, UK) and electron probe microanalysis (EPMA, EPMA-1600, Shimadzu, Japan) at room temperature. The morphology of the deposited thin films was observed by field emission scanning electron microscopy (FE-SEM, Model: JSM-6701F, JOEL, Japan). The optical transmittance of the deposited thin films was observed by UV-visible spectroscopy (Cary 100, Varian, Mulgrave, Australia). The electrical properties of the deposited thin films were characterized by Hall Effect measurements at room temperature in Van

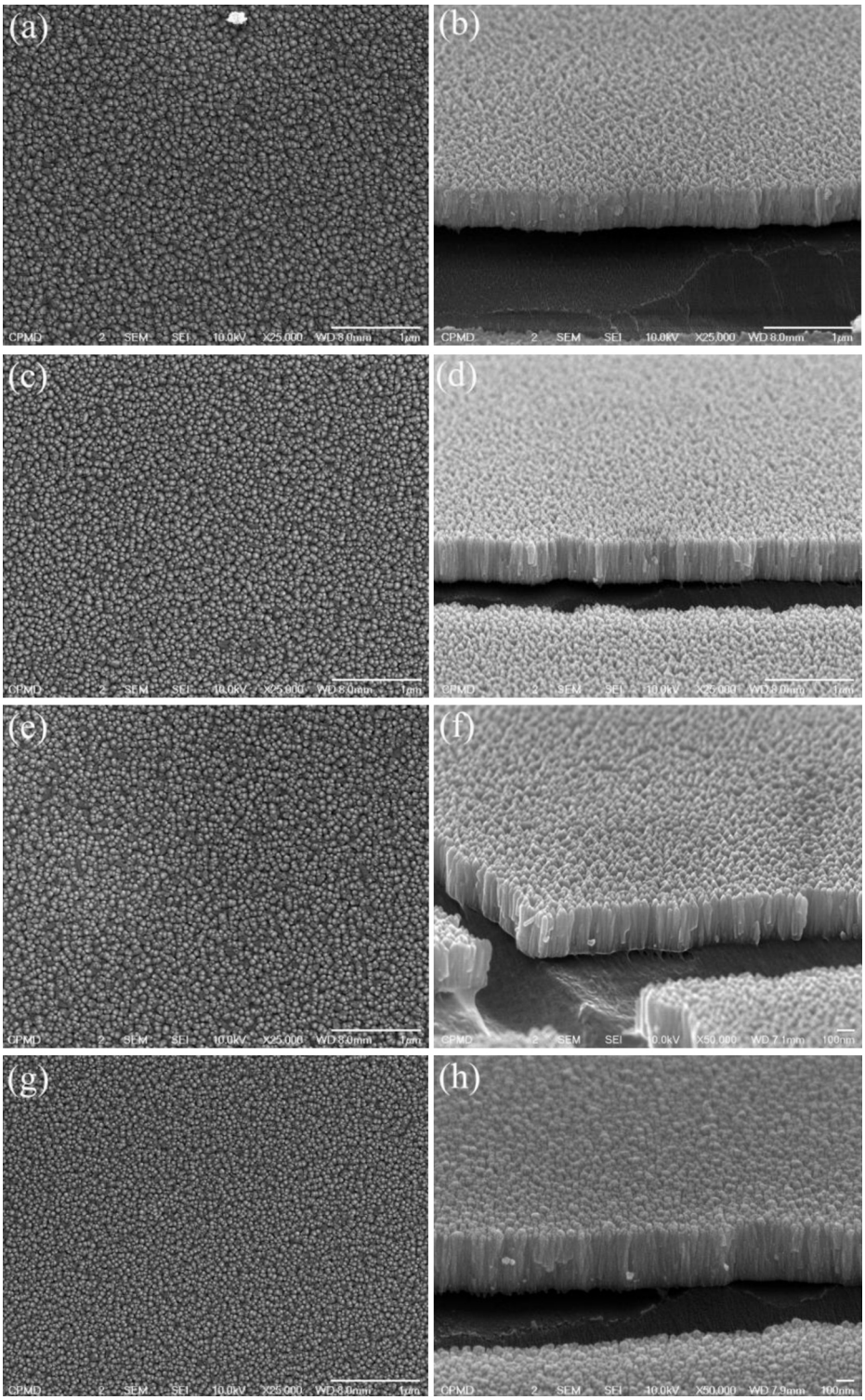

Fig. 3. Plane and cross-sectional view FE-SEM images of flexible MGZO thin films prepared with different working pressures: 4 mTorr (a and b), 6 mTorr (c and d), 8 mTorr (e and f), and 10 mTorr (g and h).

der Paw configuration (M/N #7707_LVWR, Lake Shore Cryotronics, Inc., USA).

3. Results and discussion

Fig. 1 shows the XRD patterns (a) and full width at half maximum (FWHM) values (b) of flexible MGZO thin films prepared with different working pressures. A strong peak located at 34.5° was observed in all the deposited thin film corresponding to the (0 0 0 2) plane in the ZnO crystal structure [JCPDS Card No.: 89-1297 (ZnO)]. A weak peak located at 36° was observed in the deposited thin films prepared at 6 mTorr and 8 mTorr resulting from the $(1\,0\,\bar{1}\,1)$ plane in the ZnO crystal structure, indicating that the deposited thin films were grown as a polycrystalline and

hexagonal wurtzite structure. The intensities of the (0 0 0 2) plane in the MGZO thin films were enhanced up to 6 mTorr, while they decreased with increasing working pressure. These crystal behaviors were attributed to the different sputtering yields [9]. When the thin film was deposited at low working pressure, the sputtering yield increased with increasing working pressure [9]. The increase in sputtering yield led to improved crystallinity in the deposited thin films [9]. At high working pressure, the high density of the sputtering yield provided a scattering center for sputtering atoms, resulting in poor crystallinity [9]. In addition, the diffraction angles were not significantly changed. This characteristic indicated a lack of tensile or compressive strain in the deposited thin films [11]. The peak located near 44° is attributed to the PET substrate. No other peaks from other secondary phases were observed, such as MgO, $MgGa_2O_4$, Ga_2O_3 or $ZnGa_2O_4$, nor Zn, Mg, or Ga metallic phases. Fig. 1(b) shows the FWHM values of the MGZO thin films prepared with different working pressures. The FWHM values of the MGZO thin films decreased from 0.0147° to 0.0069° at up to 6 mTorr, while that prepared at over 8 mTorr increased from 0.0118° to 0.029°. This decreased FWHM value of the MGZO thin films is attributed to the improved crystallinity.

XPS analysis of MGZO thin film was conducted to examine the changes in chemical binding, and to find the Mg and Ga elements in the MGZO crystal system. Fig. 2 shows the high-resolution XPS spectra of a typical MGZO thin film prepared at 6 mTorr, including the core level spectrum for Mg 2p (a) and Ga 2p (b). A typical survey spectrum of MGZO thin film indicates the existence of Mg, Ga, Zn, and O in the MGZO thin films, as well as C from the reference. The MGZO thin film showed a broad binding energy peak located at 50.6 eV corresponding to the electronic state of Mg 2p core levels in the MGZO compounds (Fig. 2(a)) [6]. A binding peak located at 1149.9 eV was observed in the MGZO thin films resulting from the electronic Ga $2p_{3/2}$ and $2p_{1/2}$ core levels [6]. Metallic binding energy was not observed in all the MGZO thin films. These XPS studies confirmed that Ga—O and Mg—O chemical bonds were evident without any presence of Ga and Mg metallic bonds, indicating that the Ga^{3+} and Mg^{2+} ions were perfectly substituted at Zn^{2+} sites in the MGZO crystal structure.

Fig. 3 shows FE-SEM images with plane and tilted cross-sectional views of the flexible MGZO thin films prepared with different working pressures: 4 mTorr (a and b), 6 mTorr (c and d), 8 mTorr (e and f), and 10 mTorr m (g and h). It was observed that the interfaces between the MGZO thin films and the PET substrates were very sharp without any indication of an interfacial reaction and the formation of interfacial compounds. The grains showed similar sizes ranging from 30 nm to 50 nm in all the MGZO thin films. The tilted cross-sectional FE-SEM images of all the MGZO thin films showed very dense microstructures consisting of individual grains with columnar shape.

Fig. 4 shows the variation of electrical resistivity (a), carrier concentration (b), and mobility (c) of MGZO thin films prepared with different working pressures. The electrical properties of the MGZO thin films were improved from $6.0 \times 10^{-3}\ \Omega$ cm to $5.3 \times 10^{-3}\ \Omega$ cm (resistivity) and from 1.63 $cm^2\ V^{-1}\ S^{-1}$ to 4.08 $cm^2\ V^{-1}\ S^{-1}$ (mobility) at up to 6 mTorr, while those prepared at over 8 mTorr were worse, ranging from $5.3 \times 10^{-3}\ \Omega$ cm to $1.69 \times 10^{-2}\ \Omega$ cm (resistivity) and from 4.08 $cm^2\ V^{-1}\ S^{-1}$ to 1.16 $cm^2\ V^{-1}\ S^{-1}$ (mobility). On the other hand, the carrier concentration of the MGZO thin films increased slightly from $2.2 \times 10^{20}\ cm^{-3}$ to $4.67 \times 10^{20}\ cm^{-3}$ with increasing working pressures. These electrical characteristics were strongly related to the crystallinity of the MGZO thin films. Our structural studies showed that the crystal quality of the MGZO thin films were improved at up to 6 mTorr, and greater working pressures were worse with increasing working pressures (Fig. 1). The improved crystallinity of the thin films results in a lower defect density and fewer grain boundaries than those with poor crystallinity [11]. The defects and grain boundaries acted as free electron trap centers, which reduced the charge carrier concentration and became scattering centers for electron transport, leading to a decrease in electrical mobility [7,8].

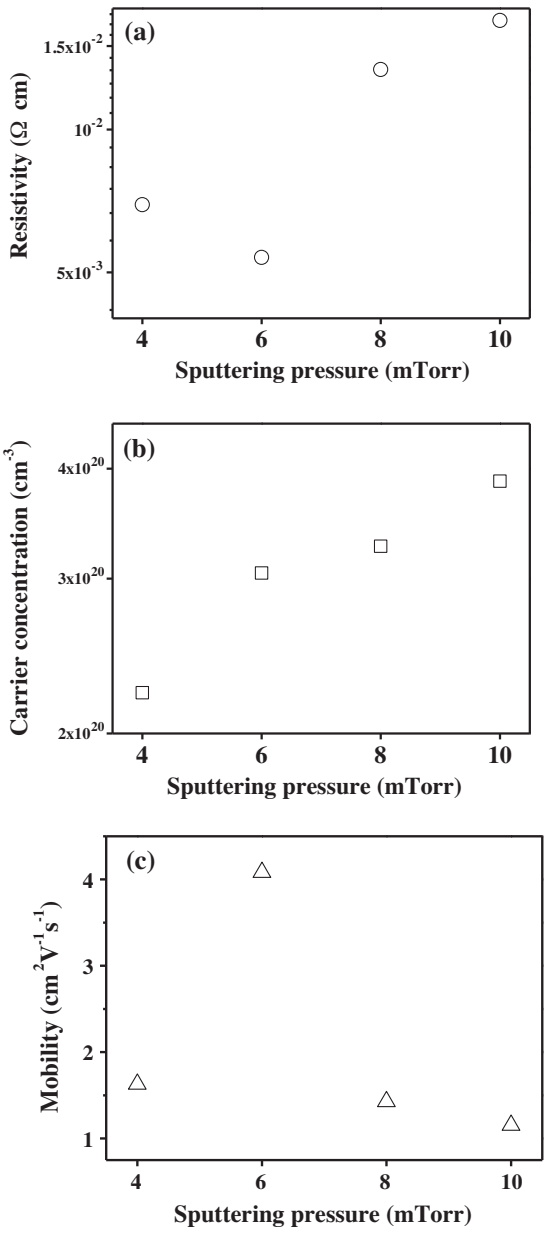

Fig. 4. Electrical resistivity (a), carrier concentration (b) and mobility (c) of flexible MGZO thin films prepared with different working pressures.

Fig. 5 shows the UV–vis transmittance spectra in the wavelength region from 300 nm to 800 nm (a) and the plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) (b) of the MGZO prepared with different working pressures. A very sharp absorption edge was observed in all the MGZO thin films, and they shifted toward a lower wavelength from 332 nm to 315 nm with increasing working pressures. This sharp absorption edge behavior was attributed to the homogeneity of grain shape, size, and low defect density in the MGZO thin films [10]. These shifts in the absorption edge were attributed to the Burstein–Moss effects, which arise from the transition energy in degenerate semiconductors due to the partially filled conduction band, and then finally improved carrier concentrations [16]. These

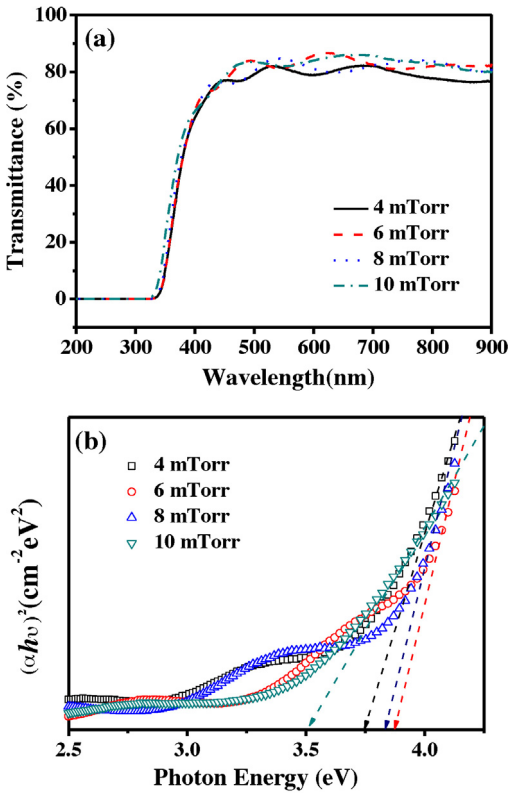

Fig. 5. UV–vis transmittance spectra in the wavelength region from 300 nm to 800 nm of MZO (a) and MGZO (b) and the plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) of flexible MGZO thin films prepared with different working pressures.

optical characteristics were in good agreement with improved carrier concentration (Fig. 4(b)). The optical transmittances in all the MGZO thin films were estimated to be in the range of 75–85% in the visible region. The optical band gap energy of MGZO thin films was measured by a linear extrapolation on the *x*-axis of plot of the $(\alpha h\nu)^2$ vs. photon energy ($h\nu$). The band gap energy values of the films were found to be strongly dependent on the working pressures (Fig. 5(b)). The optical band gap energy of MGZO thin films increased from 3.5 eV to 3.91 eV with increasing working pressures. This optical band gap behavior was in good agreement with the Burstein–Moss effects, such as the increase in carrier concentration and the shift toward a low wavelength for the absorption edge.

These results suggest that the flexible ZnO-based thin films with outstanding optical and electrical properties were successfully prepared by introducing Mg and Ga in the ZnO crystal structure. These flexible MGZO thin films with outstanding characteristics can be easily applied to flexible electro-optical devices.

4. Conclusion

The wide band gap characteristics of quaternary and flexible MGZO thin films were successfully prepared on PET substrate by RF sputtering technique. The structural, morphological, electrical and optical characteristics of the MGZO thin films were found to be strongly dependent on the working pressures. A low electrical resistivity of $5.3 \times 10^{-3}\,\Omega\,cm$ and wide band gap energy of 3.91 eV can be developed in the ZnO-based thin films by introducing Mg and Ga to the ZnO structure. These flexible MGZO thin films with wide band gap energy and low electrical resistivity are promising TCO material candidates for flexible optoelectronic devices.

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